歐文日本化學會誌　第一卷第五號

大正十五年五月二十五日印刷
大正十五年五月二十八日發行

編輯兼發行者　東京帝國大學理學部內　松原行一

印刷者　東京市日本橋區兜町二番地　神谷岩次郎

發行所　東京帝國大學理學部內　日本化學會事務所

印刷所　東京市日本橋區兜町二番地　東京印刷株式會社

賣捌所　東京市日本橋區通三丁目十四番地　丸善株式會社

A SIMPLE MANOMETER FOR MEASURING LOW PRESSURES[1].

By Toshiaki SHIRAI.

Received March 20, 1926. Published June 28, 1926.

According to the kinetic theory of gas, the heat conductivity of a gas is independent of its pressure. This fact was verified experimentally by observing the cooling velocity of a body which is kept in the gas. Thus the time which is required to cool from a given temperature to another under a constant condition, is independent of the pressure of the surrounding gas. But this rule holds only within a limited range of pressures. Under high pressures it is disturbed by the convection of gas and by other phenomena. And at the pressures lower than few millimetres of mercury, longer time is required for the cooling of the same temperature range under the same condition. This fact was first observed by Kundt and Warburg,[2], and was attributed to the discontinuity of the temperature gradient, which grows prominent at the boundary of the solid and gas, as the pressure diminishes.

Such a behavior of rarefied gas is sometimes utilised as the measure of its pressure. Pirani's manometer[3] and Rohn's manometer[4] belong to this type. Since then many improvements were reported[5]. The manometers of this type do not directry show the pressure, as Mc Leod manometer does, so we must calibrate them with known pressures. They are, however, free from mercury vapour, the existence of which will prevent the correct reading of the pressure, and moreover proves to be a hindrance to the perfect evacuation. Another great defect of Mc Leod manometer is that it cannot be used to measure the pressures of easily condensible vapours. For these reasons, in many cases, more complicated manometers such as those described above are used in place of the Mc Leod manometer.

Experimental. Here we describe another substitute for Mc Leod manometer, which is more simple and far less expensive than all other manometers. The construction of it is shown by *M* in Fig. 1. A thermometer

(1) Read before the Chemical Society of Japan, April, 1924.
(2) Kundt and Warburg, *Pogg. Ann.*, 156 (1875), 177.
(3) Pirani, *Verh, d. D. Phys. Ges.*, 8 (1906), 686.
(4) Rohn, *Z. Electrochem., Sec.*, 20 (1914), 534.
(5) Hale, *Trans. Amer. Electrochem., Soc.*, 20 (1911), 234.
Sô, *Proc. Tokyo Math. Phys. Soc., 3rd. Series*, 1 (1919), 152.
Campbell, *Proc. Phys. Soc. London*, 33 (1921), 287.

is fixed in a tube, which is specially so constructed that it has long cylindrical mercury bulb, and graduated to indicate one tenth of a degree. The thermometer should not be deformed by pressure change, and it is more prefarable that it is as sensitive as possible. These two contradictory requirements considerably restrict the sensitiveness of this manometer.

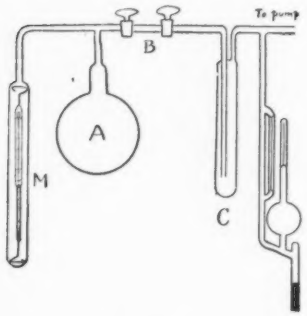


Fig. 1.

Now this apparatus, as already described, must be calibrated with known pressures. The pressures below to few tenth of a millimetre were compared with a Mc Leod manometer. For the pressures lower than these, a pipette system has been used which is shown in Fig. 1. The volumes of the spaces $M+A$ and B are known. At first the spaces A, B and M were thoroughly evacuated and then charge B with a gas of known pressure, and let it expand into A, M and B. As these volumes are known we can easily calculate the pressure after expansion of the gas. During evacuation the mercury trap C is cooled by liquid air to prevent the invasion of mercury vapour into the system. At a known pressure, the cooling velocity of the thermometer is measured by the following manner.

At first, M is warmed, and then suddenly envelop it with a bath of lower constant temperature. Now the thermometer begins to cool, and the time required to cool from a given temperature to the other is measured. It may be convenient to choose 0°, of melting ice, for the temperature of the bath. But in the present experiment, as the graduation of thermometer was from 30° to 42°, the cooling bath of 25° was used, and measured the time required to cool the thermometer from 39° to 32°. Limiting the range of the operating temperature narrower, we can well express the cooling velocity with the Newton's law of cooling, consequently we can easily calculate the requiring time even when we failed to measure the time of cooling for the given temperature range or when the thermostat was not exactly fixed at 25°. The Newton's law is

$$-\frac{dT}{dt} = k'(T-T_0), \quad \cdots\cdots(1)$$

or

$$t = k' \log \frac{T_1-T_0}{T_2-T_0}, \quad \cdots\cdots(2)$$

where t is the time required to cool from a temperature T_1 to another temperature T_2, T_0 is the temperature of the bath and k' is a constant depending on the pressure.

The cooling times obtained under various pressures are plotted against pressure in Fig. 2. As each gas has its own heat conductivity, different curves are obtained for different gases. The curves given are those for air and hydrogen.

If such curves were drawn for an apparatus, we can use it as a manometer. Now to construct these curves we must make troublesome measurements. But as is shown in the following pages, if we use a thermometer of long cylindrical mercury bulb, and limit the operating temperature range narrow enough, this pressure-time relation can be expressed in the following form:

$$p = k\,\frac{t_0 - t}{t - t_{760}} \qquad \cdots\cdots(3)$$

where t is the cooling time when the pressure is p, t_0 and t_{760} are the cooling times for the highest vacuum

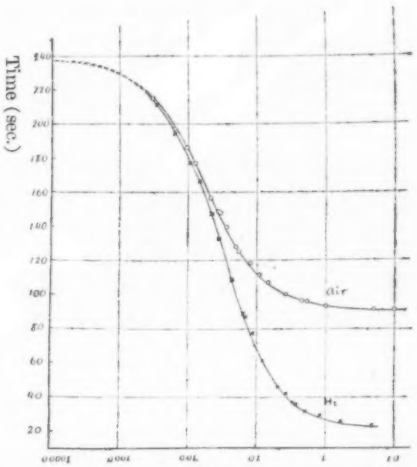


Fig. 2. Pressure (mm. in log. scale)

Air			Hydrogen		
p mm.	t sec.	$k = p\frac{t - t_{760}}{t_0 - t}$	p mm.	t sec.	$k = p\frac{t - t_{761}}{t_0 - t}$
760.	90.5 ($=t_{760}$)		770.	20.9 ($=t_{761}$)	
250.	90.5		223.	20.9	
26.	90.5		50.	21.0	
15.5	90.6		18.	21.3	
5.0	90.9		5.0	22.6	
1.8	91.0		1.62	25.1	
1.01	92.8		0.78	29.0	0.0295
0.52	95.5	0.0183	0.55	31.8	0.0291
0.43	95.9	0.0172	0.382	36.3	0.0292
0.262	100.0	0.0181	0.380	36.7	0.0299
0.145	107.2	0.0169	0.265	42.6	0.0296
0.108	110.7	0.0171	0.222	41.5	0.0285
0.0809	118.0	0.0185	0.124	61.0	0.0282
0.0540	124.2	0.0160	0.0860	76.5	0.0296
0.050	127.7	0.0186	0.0630	86.8	0.0285
0.0375	139.0	0.0185	0.0645	87.3	0.0286
0.0280	147.5	0.0177	0.0430	108.2	0.0290
0.0270	148.0	0.0173	0.0271	132.9	0.0290
0.0212	156.0	0.0171	0.0215	140.9	0.0267
0.0124	177.0	0.0177	0.0143	165.3	0.0285
0.00934	185.7	0.0172	0.0106	177.0	0.0274
0.00623	197.4	0.0163	0.00714	194.1	0.0285
0.00312	210.0	0.0136	0.00357	210.9	0.0255
0.0000	237.5 ($=t_0$)	—	0.0000	237.5 ($=t_0$)	—
		mean 0.01759			mean 0.02874

and 760 mm. respectively and k is a constant depending upon the nature of the gas and the dimentions of the apparatus. The experimental results are shown in the above table, together the values of k calculated therefrom. The curves in Fig. 2 represent these results.

Theoretical. Smoluchowski[1] introduced a quantity γ under the name of "Temperatursprungskoeffizient", having the following relation,

$$T' - T = \gamma \frac{\partial T'}{\partial n} \quad \cdots\cdots(4)$$

where T is the temperature of the solid at the boundary, T' is that of the gas contacting to it, n is a normal drawn at the boundary surface inwards to the gaseous space, and γ is a proportionality constant. He has known experimentally that the quantity γ is proportional to the mean free path of the gas. Now, as the mean free path is inversely proportional to the pressure p, we can express this relation as follows,

$$\gamma p = \text{constant} \quad \cdots\cdots(5)$$

This shows that if p decreases γ becomes larger, consequently $T' - T$ becomes larger and $\frac{\partial T'}{\partial n}$ smaller. Under the pressures higher than few millimetres γ is negligibly small, so we cannot find any difference botween T and T', and there exists no cause that prevents the heat transmission through the boundary.

Assuming that the cylindrical mercury bulb of radius r_1, and the outer tube of radius r_2 are coaxial, and moreover we consider another coaxial cylinder between them, whose radius is r. Then, as the bulb is long, we may assume that there is no heat loss from the ends of the bulb. The heat transmission at the side of cylinder takes place in two ways, a part by conduction, which depends upon the conductivity of the gas $\varkappa$. temperature gradient $(\partial T''/\partial r)$ at this point, and the surface area of this cylinder $2\pi rl$, the other part by radiation, which can be regarded to be propartional to the difference of the temperature of the thermometer and that to the bath $(T - T_0)$, when the range of the operating temperature is narrow, otherwiese it obeys Stefan-Boltzmann's law.

Now in a unit time the thermometer bulb will lose the heat quantity $-C\frac{dT}{dt}$, so the following relation will be obtained;

$$-C\frac{dT}{dt} = -\varkappa \frac{\partial T'}{\partial r} 2\pi rl + A'(T - T_0) \quad \cdots\cdots(6)$$

(1) Smoluchowski, *Ann. d. Phys. u. Chem.*, **64** (1898), 101.

Comparing (6) with (1), we obtain,

$$-\frac{dT}{dt} = (B+A')(T-T_0) \quad \cdots\cdots(7)$$

where $A' = -\frac{A}{C}$, $\quad B = -\varkappa 2\pi r l \frac{\partial T'}{\partial r}\frac{1}{C}\frac{1}{T-T_0}$, and $\quad k' = B+A'$.

As $\varkappa$, π, l, T_0 and C are constants, moreover T is constant at a moment, $\frac{\partial T'}{\partial r} r$ must also be constant at the moment, or

$$r\frac{\partial T'}{\partial r} = a \quad \cdots\cdots(8)$$

This expression shows the distribution of temperatures of the gas from r_1 to r_2 at that moment; and the difference of the temperatures at r_1 and r_2 is given by

$$T'_{r_1} - T_{r_2} = a \log \frac{r_1}{r_2} \quad \cdots\cdots(9)$$

From the relation (4)

$$\left.\begin{aligned} T'_{r_1} - T &= \gamma\left(\frac{\partial T'}{\partial r}\right)_{r_1} \\ T_0 - T_0 &= -\gamma\left(\frac{\partial T'}{\partial r}\right)_{r_2} \end{aligned}\right\} \quad \cdots\cdots(10)$$

Comparing these with (8), we get

$$\frac{T'_{r_1}-T}{\gamma} r_1 = \frac{T_0 - T'_{r_2}}{\gamma} r_2 = a$$

or

$$\left.\begin{aligned} T'_{r_1} - T &= a\gamma\frac{1}{r_1} \\ T_0 - T'_{r_2} &= a\gamma\frac{1}{r_2} \end{aligned}\right\} \quad \cdots\cdots(11)$$

From (9) and (11) we obtain,

$$T_0 - T - a\log\frac{r_1}{r_2} = a\gamma\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$$

or

$$a = \frac{T_0 - T}{\gamma\left(\frac{1}{r_1}+\frac{1}{r_2}\right)+\log\frac{r_1}{r_2}} \quad \cdots\cdots(12)$$

Then

$$B = -\frac{\varkappa 2\pi l}{C}\frac{1}{\gamma\left(\frac{1}{r_1}+\frac{1}{r_2}\right)+\log\frac{r_1}{r_2}} \quad \cdots\cdots(13)$$

By equation (5), this can be written in the form :

$$B = \frac{1}{\frac{a}{p} + b} \quad \cdots\cdots(14)$$

where $a = \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \frac{C}{2\pi l} \times \text{constant}$, and $b = \log \frac{r_1}{r_2} \frac{C}{\varkappa 2\pi l}$.

Now the integral form of (7) is

$$\log \frac{T_1' - T_0}{T_2' - T_0} = (B + A')\, t \quad \cdots\cdots(15)$$

In the perfect vacuum no conduction takes place, so $B = 0$, therefore

$$\log \frac{T_1' - T_0}{T_2' - T_0} = A'\, t_0 \quad \cdots\cdots(16)$$

From (14), (15) and (16) we obtain,

$$\left(\frac{1}{t} - \frac{1}{t_0}\right) A'\, t = \frac{1}{\frac{a}{p} + b} \quad \cdots\cdots(17)$$

If p is larger than few millimetres of mercury, then the value of a/p may be neglected to b, and the following relation will be obtained,

$$\left(\frac{1}{t_{760}} - \frac{1}{t_0}\right) A'\, t = \frac{1}{b} \quad \cdots\cdots(18)$$

Substituting the value of b from (18) to (17),

$$\frac{1}{\left(\frac{1}{t} - \frac{1}{t_0}\right) A'\, t_0} = \frac{a}{p} \frac{1}{\left(\frac{1}{t_{760}} - \frac{1}{t_0}\right) A'\, t_0}$$

or

$$\frac{a}{p} A' = \frac{t_0}{t_0 - t_{760}} \frac{t - t_{760}}{t_0 - t}$$

Putting

$$k = \frac{t_0 - t_{760}}{t_0}\, a.\, A'$$

in the above equation, we obtain the relation (3),

$$p = k \frac{t_0 - t}{t - t_{760}}.$$

Summary.

A simple all glass manometer, which can be used for measuring the pressures from 0.1 mm. to 0.001 mm. has been described. The manometer

consists of a thermometer enclosed in a tube. The pressure measurement is done by measuring the time required to cool the thermometer from a given temperature to the other under a given condition. Using a thermometer of long mercury bulb and limiting the operating temperature range so narrow that the Newton's law of cooling holds, we get the following relation :

$$p = k\,\frac{t_0 - t}{t - t_{760}}.$$

This relation was well confirmed by experiments using the air and the hydrogen.

In conclusion I wish to express my hearty thanks to Prof. J. Sameshima, under whose guidance the present investigation was carried out.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

ON THE ANOMALOUS DISPERSION AND ABSORPTION OF ELECTRIC WAVES. III.

By San-ichiro MIZUSHIMA.

Received April 9, 1926. Published June 28, 1926.

With the electric wave of 9.5 metres, the measurements were carried out as the continuation of previous experiments.[1] The results obtained for monovalent alcohols are shown in the following tables.

ΔC : Displacement of glass plate,

$\Delta C'$: Corrected value of ΔC,

I/I_0 : Ratio of the deflections of the galvanometer at resonance,

ε : Dielectric constants,

K : Electric conductivity which is equivalent to anomalous absorption (cm^{-1} ohm^{-1}).

References : L.—Landolt u. Jahn, *Z. physik. Chem.* **10** (1892), 289.
A.—Abegg, *Wied. Ann.*, **60** (1897), 54.
A.S.—Abegg u. Seitz, *Z. physik. Chem.*, **29** (1899), 242.
T.—Turner, *Z. physik. Chem.* **35** (1900), 385.
W.—Walden, *Z. physik. Chem.*, **70** (1909), 569.

(1) Mizushima, This journal, **1** (1926), 47 & 83.

TABLE 1. Methyl alcohol.

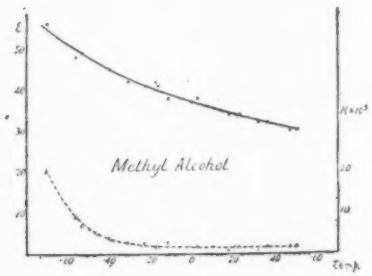
Vessel.	Temp.	ΔC	I/I_0	$\Delta C'$	ε	$K \times 10^5$	ε (Other authors)
II	50	4.35	.58	4.35	30	2	
II	47	4.4	.58	4.4	30	2	
IV	46	5.7	.56	5.7	30	2	
II	36	4.7	.58	4.7	32	2	
III	31	5.4	.57	5.4	32	1	
IV	31	6.25	.59	6.25	32	1	
II	22	5.1	.58	5.1	34	2	
III	20	5.85	.56	5.85	34	2	
IV	17	6.8	.60	6.8	34	1	
—	13.4	—	—	—	—	—	35.3 (L.)
II	2	5.85	.56	5.85	38	2	
—	0	—	—	—	—	—	35.0 (A.S.)
	− 1	4.65	.58	4.65	37	2	
I	−12	4.85	.53	4.85	38	3	
II	−17	6.4	.50	6.4	41	2	
II	−18	6.6	.50	6.6	42	2	
I	−23	5.25	.51	5.25	41	3	
I	−31	5.5	.48	5.5	42	3	
I	−40	5.9	.40	5.9	45	4	
—	−50	—	—	—	—	—	45.3 (A.S.)
I	−53	6.55	.28	6.55	49	7	
I	−56	6.55	.24	6.55	48	9	
II	−70	9.6	.08	9.25	56	20	

TABLE 2. Ethyl alcohol.

Vessel.	Temp.	$\Delta C'$	I/I_0	$\Delta C'$	ε	$K \times 10^5$	ε (Other authors)
I	54	2.35	.80	2.35	20.5	—	
II	53	2.9	.75	2.9	20	—	
—	50	—	—	—	—	—	20.5 (W.)

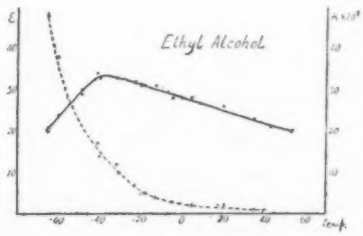
TABLE 2. *Continued.*

Vessel.	Temp.	ΔC	I/I_1	$\Delta C'$	ε	$K \times 10^5$	ε (Other authors)
II	43	3.1	.70	3.1	21	1	
I	35	2.7	.74	2.7	23	1	
II	20	3.85	.56	3.85	25	2	25.8 (A.S.)
I	17	3.05	.67	3.05	25	2	
—	14.7	—	—	—	—	—	25.8 (T.)
I	4	3.4	.58	3.4	28	2	
—	0	—	—	—	—	—	28.4 (A.S.)
I	− 5	3.5	.54	3.5	28	3	
I	−13	3.85	.46	3.85	31	4	
I	−18	4.0	.36	4.0	31	5	
I	−20	3.9	.35	3.9	31	5	
I	−23	4.05	.30	4.05	32	7	
I	−32	4.35	.18	4.3	33	12	
I	−40	4.4	.16	4.3	33	14	35.3 (A.S.)
I	−41	4.55	.14	4.45	34	17	
II	−49	5.25	.05	4.6	29	29	
I	−49	4.4	.07	3.9	30	29	
I	−60	3.85	.05	3.15	24	38	
I	−65	3.6	.04	2.75	21	48	
II	−65	4.55	.03	3.15	20	48	



×.....Value of ε
△.....Value of K

Fig. 1.



×.....Value of ε
△.....Value of K

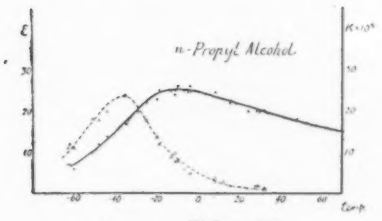
Fig. 2.

TABLE 3. Propyl alcohol.

Vessel.	Temp.	ΔC	I/I_0	$\Delta C'$	ε	$K\times10^5$	ε (Other authors)
I	70	1.7	—	1.7	15	—	
IV	48	3.35	.76	3.35	18	<1	
IV	32	3.85	.64	3.85	20	1	
IV	29	3.85	.50	3.85	20	2	
I	29	2.3	.60	2.3	20	2	
I	28	2.35	.61	2.35	20	2	
I	24	2.35	.69	2.35	20	1	
—	20	—	—	—	—	—	22.2 (A.S.)
IV	15	4.35	.43	4.35	22	2	
—	14.3	—	—	—	—	—	22.4 (L.)
IV	8	4.9	.33	4.9	24.5	3	
IV	8	4.9	.30	4.9	24.5	4	
—	0	—	—	—	—	—	24.8 (A.S.)
IV	− 4	5.3	.24	5.3	26	5	
III	− 7	4.3	.22	4.3	25	6	
IV	−10	5.35	.16	5.25	26	8	
III	−11	4.45	.18	4.4	25	8	
IV	−11	5.05	.13	4.9	24	10	
IV	−13	5.35	.14	5.2	25	9	
III	−19	4.7	.12	4.5	25	12	
I	−20	3.05	.16	2.95	23	14	
IV	−25	5.0	.07	4.5	22	18	
III	−29	4.15	.07	3.65	21	20	
I	−35	2.55	.09	2.1	17	24	
III	−44	3.0	.07	2.5	14	20	
III	−48	2.45	.08	2.05	12	18	
IV	−51	2.45	.07	1.95	10	18	
III	−60	1.1	.14	0.95	6	11	33.7 (A.S.)
	−62	0.9	.18	0.85	7	12	
IV	−63	1.5	.12	1.3	7	11	

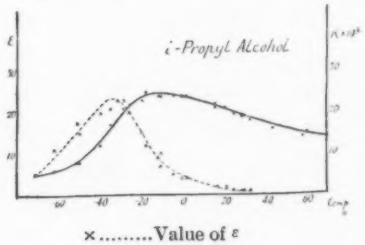
TABLE 4. Isopropyl alcohol.

Vessel.	Temp.	ΔC	I/I_0	$\Delta C'$	ε	I/I_0
III	70	2.2	—	2.2	14	<1
III	60	2.4	.83	2.4	15	<1
II	59	2.0	.86	2.0	14	<1
III	43	2.6	.78	2.6	16	<1
III	32	3.0	.68	3.0	18	1
II	31	2.65	.76	2.65	18.5	<1
III	29	3.1	.65	3.1	19	1
II	29	2.7	.67	2.7	19	1
III	28	3.15	.67	3.15	19	1
III	24	3.25	.59	3.25	19.5	1
IV	20	4.1	.48	4.1	21	2
III	15	3.65	.50	3.65	22	2
II	15	3.15	.47	3.15	21	2
III	1	4.05	.33	4.05	24	4
IV	− 1	4.9	.28	4.9	24	4
III	− 5	4.15	.24	4.15	24	5
III	−11	4.25	.20	4.25	24	7
II	−11	3.75	.17	3.65	24	10
IV	−12	5.05	.15	4.95	24	9
III	−18	4.65	.12	4.45	25	12
III	−20	4.4	.10	4.1	23	15
II	−26	3.75	.08	3.4	22	20
III	−29	4.25	.06	3.65	21	23
III	−32	3.75	.06	3.15	18	23
III	−35	3.65	.05	2.95	17	26
IV	−40	2.9	.06	2.25	12	20
III	−50	1.65	.10	1.35	8	15
II	−51	1.5	.10	1.2	8	17
III	−62	1.1	.13	0.9	6	11
II	−71	0.7	.30	0.7	5	5



×.....Value of ε
△.....Value of K

Fig. 3.



×.....Value of ε
△.....Value of K

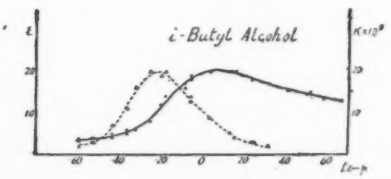
Fig. 4.

TABLE 5. Isobutyl alcohol.

Vessel.	Temp.	ΔC	I/I_0	$\Delta C'$	ε	$K\times10^5$	ε (Other authors)
IV	66	2.4	.90	2.4	13	<1	
III	53	2.15	.81	2.15	13.5	<1	
IV	51	2.8	.84	2.8	15	<1	
III	40	2.55	.70	2.55	15.5	<1	
IV	31	3.3	.58	3.3	17	2	
IV	24	3.5	.40	3.5	18	3	
III	23	3.05	.40	3.05	18	3	
III	22	3.0	.40	3.0	18	3	
—	18	—	—	—	—	—	18.9 (T.)
III	15	3.8	.27	3.8	20	4	18.7 (L.)
IV	14	3.3	.34	3.3	20	4	
III	14	3.35	.29	3.35	20	4	
III	13	3.45	.26	3.45	20	5	
IV	12	4.0	.25	4.0	20	4	
IV	3	4.1	.15	4.0	20	9	
—	0	—	—	—	—	—	21.8 (A.S.)
III	− 6	3.45	.11	3.2	19	14	
IV	− 6	3.85	.11	3.6	18	13	
IV	− 9	3.8	.08	3.4	17	16	
III	−18	2.85	.07	2.35	14	20	
III	−20	2.4	.07	1.95	12	19	
IV	−25	2.1	.06	1.45	8	20	
III	−32	1.25	.09	0.9	6	16	
III	−36	1.0	.13	0.85	6	11	
IV	−36	1.1	.12	0.9	5	11	
—	−40	—	—	—	—	—	27.0 (A.S.)
III	−43	0.75	.20	0.7	5	7	
IV	−43	0.8	.18	0.7	4	7	
III	−52	0.55	.34	0.55	4	3	
IV	−53	0.6	.37	0.6	4	3	
III	−59	0.5	.48	0.5	4	2	
IV	−59	0.55	.44	0.55	3	2	

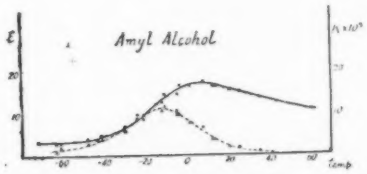
TABLE 6. Amyl alcohol.

Vessel.	Temp.	ΔC	I/I_0	$\Delta C'$	ε	$K\times10^5$	ε (Other authors)
IV	61	2.05	.88	2.05	11	<1	
III	60	1.7	.81	1.7	11	<1	
III	43	2.05	.72	2.05	13	<1	
IV	35	2.7	.63	2.7	14	1	
IV	25	2.95	.48	2.95	15.5	2	
II	20	2.3	.46	2.3	16	2	16.0 (A.S.)
—	13.8	—	—	—	—	—	16.6 (L.)
III	13	2.8	.30	2.8	17	4	
II	12	2.5	.34	2.5	17	4	
I	7.5	2.15	.30	2.15	18	7	
IV	1	3.25	.16	3.25	17	8	
—	0	—	—	—	—	—	17.4 (A.S.)
I	− 4	2.05	.22	2.05	17	10	
IV	− 5	3.2	.12	3.0	15	11	
III	− 5	2.75	.15	2.6	15	10	
II	−11	2.35	.14	2.2	15	12	
III	−12	2.35	.13	2.15	13	11	
IV	−12	2.65	.11	2.45	13	11	
III	−21	1.7	.15	1.55	9	10	
IV	−21	1.85	.13	1.7	9	10	
	−24	1.2	.23	1.2	10	9	
II	−30	0.95	.24	0.95	7	7	
IV	−30	1.1	.20	1.1	6	6	
I	−41	0.5	.42	0.5	5	4	
I	−43	0.4	.45	0.4	4	4	
II	−48	0.45	.44	0.45	4	3	
—	−50	—	—	—	—	—	23.0 (A.S.)
II	−61	0.3	.60	0.3	3	2	
I	−63	0.2	.74	0.2	3	1	



×.....Value of ε
△.....Value of K

Fig. 5.



×.....Value of ε
△.....Value of K

Fig. 6.

Table 7 contains the values of ε and K at every tenth degree of temperature obtained by graphical interpolation from the above results.

TABLE 7.

Temp.	Acetone	Glycerine		Methyl alcohol		Ethyl alcohol		Propyl alcohol		Isopropyl alcohol		Isobutyl alcohol		Amyl alcohol	
	ε	ε	$K\times10^5$	ε	$K\times10^5$	ε	$K\times10^5$	ε	$K\times10^5$	ε	$K\times10^5$	ε	$K\times10^5$	ε	$K\times10^5$
70	—	35	<1	—	—	—	—	15	<1	14	<1	—	—	—	—
60	—	37	1	—	—	—	—	16	<1	15	<1	14	<1	11	<1
50	—	39	2	30	2	21	<1	17	<1	16	<1	15	<1	12	<1
40	—	40	4	31	2	22	1	19	<1	17	<1	16	<1	13	1
30	—	42	8	33	2	23	1	20	1	19	1	17	2	15	1
20	22	41	15	34	2	25	1	22	2	21	1	19	3	16	2
10	23	34	25	35	2	27	2	23	3	22	3	20	6	18	5
0	24	20	26	37	2	28	2	25	5	24	5	20	10	17	9
−10	25	12	12	39	2	30	4	25	8	25	8	17	15	15	11
−20	26	8	4	40	2	31	6	24	14	24	15	11	20	10	10
−30	27	5	2	42	3	33	10	20	22	19	23	7	17	7	7
−40	28	4	1	45	4	33	15	15	23	13	22	5	9	5	4
−50	29	4	<1	48	7	29	23	10	18	8	16	4	4	4	3
−60	30	4	<1	51	12	24	36	7	12	6	10	4	2	4	2
−70	31	4	<1	55	20	—	—	—	—	5	5	—	—	3	1

The behaviours of propyl, isopropyl, isobutyl, and amyl alcohols are, in general, quite similar to that of glycerine. At higher temperatures there is only little absorption and the values of ε obtained are found to be in good agreement with those measured at longer waves. As the temperature is gradually lowered, both ε and K increase, till each of them reaches its maximum respectively. The maximum of K lies at the point where the temperature coefficient of ε is nearly maximum. (See figures). At still lower temperatures, the values of K are decreasing and those of ε approaching to the square of the refractive indices for the visible light.

For ethyl alcohol, only the maximum of ε is obtained, and for methyl both of the maxima are not found. But it may be granted that at sufficiently low temperatures they will also behave as other alcohols.

As given above these alcohols show anomalous absorptions of the electric wave of the wave length of 9.5 metres as well as 6.1 metres, and these absorptions are incomparably greater than those expected from their electric conductivities. Anomalous changes of dielectric constants are observed at the same time. The point of maximum absorption lies always at the

temperature at which the temperature coefficient of the anomalous change of ε is nearly maximum. The value of ε at this point is nearly equal to the mean of the dielectric constant at long wave lengths and the square of the refractive index for the visible light. From this fact it can evidently be expected that if the change of ε by the wave length be studied at constant temperature, the point of the maximum change of ε (i. e. the point where the dispersion is most anomalous) will be accompanied by a very strong absorption of the wave. Experiments are now continued with waves of different wave lengths in order to obtain the data necessary for the study of the above relation and its analogy to that between the anomalous dispersion and absorption of the visible light.

The author wishes to express his best thanks to Prof. M. Katayama for his kind guidance.

October 31, 1925,
Laboratory of Physical Chemistry,
Faculty of Science, Tokyo Imperial University.

MELTING CURVES OF THE SYSTEMS HYDROGEN CHLORIDE–ETHYL ETHER AND HYDROGEN CHLORIDE–ACETONE.

By **Masao HIRAI.**

Received April 30, 1926. Published June 28, 1926.

Melting curves of the system hydrogen chloride- ethyl ether was already studied by O. Maass and D. McIntosh[1] in 1913. These authors obtained a result that there exists three compounds $(HCl)(C_4H_{10}O)$, $(HCl)_2(C_4H_{10}O)$, and $(HCl)_5(C_4H_{10}O)$. I have recently studied this system again, together the system hydrogen chloride-acetone, and are described in the following.

The System Hydrogen Chloride–Ethyl Ether. A small quantity of pure dehydrated ether is introduced into a glass bulb of about 1.5 c.c. capacity and weighed. The bulb is then connected to a reservoir of pure dry hydrogen chloride gas, and cooled by liquid air. The hydrogen chloride condenses into the bulb, the quantity of which can roughly be estimated by the pressure change and the volume of the gas reservoir. The bulb is, then, hermetically sealed and is put in a bath of low temperature. The bath is made of a non-silvered Dewar vessel containing petroleum ether, which is cooled by

(1) Maass and McIntosh, *J. Am. Chem. Soc.*, **35** (1913), 537.

dropping liquid air. The melting of the mixture in the bulb can be seen from the outside of the vessel, and the temperature was measured by three series copper-constantan thermocouples which is kept by the side of the bulb.

The composition of the mixture was determined in the following manner. The bulb is taken out after the melting point was observed, and brought into a thick walled glass bottle which containing some water in it. The bottle is, then, shaken vigorously so that the bulb is broken and the hydrogen chloride gas is absorbed by the water. The hydrochloric acid solution thus produced is then titrated with alkali solution.

The results of the experiments are as follows.

Mol % of HCl.		Melt. pt.	Mol % of HCl.		Melt. pt.
0	(pure ether)	−117.7°	63.71		− 87.4°
10.84		−118.8	68.30		− 89.0
13.07		−119.3	72.61		− 93.5
20.32		−124.2	78.94		−100.4
22.67		−127.8	81.24		−104.0
31.96		−126.5	88.80		−113.5
36.34		−115.4	89.45		−115.5
40.45		−110.9	93.92		−123.6
47.87		−100.4	94.24		−123.7
49.03		−100.9	95.35		−120.8
52.82		−107.3	96.13		−120.5
55.16		− 94.5	100.00	(pure HCl)	−112.5
61.76		− 89.3			

Graphically it becomes as Fig. 1. From this figure it is evident that there exists only one compound $(HCl)_2(C_4H_{10}O)$ which melts at −87.3°.

The System Hydrogen Chloride–Acetone. The experimental procedure is quite same as the system mentioned above. The results are as follows.

Mol % of HCl.		Melt. pt.	Mol % of HCl.	Melt. pt.
0	(pure acetone)	− 94.5°	45.12	−81.7
14.43		−107.0	52.91	−80.0
20.50		−111.4	55.56	−82.7
27.29		−114.6	57.26	−86.6
31.78		−104.2	60.39	−92.8
42.99		− 85.7		

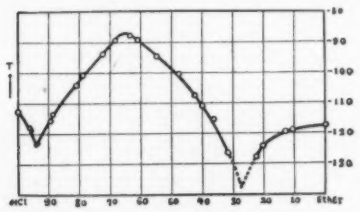


Fig. 1.

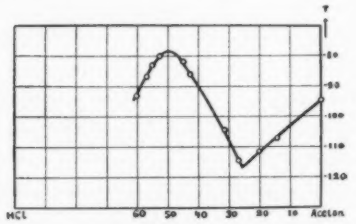


Fig. 2.

Graphically it becomes as Fig. 2. In this case, there is one compound (HCl) (C_3H_6O), whose melting point is −79.0°. In the part where the amount of hydrogen chloride exceeds 60 percent, the mixture became glassy mass by cooling and could not determine the melting point.

The author's thanks are due to Prof. J. Sameshima for his kind guidance.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

SYNTHESIS OF METHOXY-HYDROXY-N-METHYL-3·4-DIHYDROISOQUINOLINIUM SALTS.

By Shirō AKABORI.

Received April 7, 1926. Published June 28, 1926.

(Continued from Page 102)

6-Methoxy-7-hydroxy-2-methyl-3·4-dihydroisoquinolinium Salts (VIII). 1 gram of 6-methoxy-7-benzyloxy-2-methyl-3·4-dihydroisoquinolinium chloride and 3 c.c. of concentrated hydrochloric acid were slightly warmed on a water-bath. The solution became gradually opaque and finally deposited oily drops of benzyl chloride. When the solution was separated from benzyl chloride and evaporated in a vacuum over potassium hydroxide, 6-methoxy-7-hydroxy-2-methyl-3.4-dihydroisoquinolinium chloride (VIII) remained as a crystalline mass. This was recrystallized from a mixture of methyl alcohol and acetone, from which it was deposited in the form of yellow glistening plates. It melts and decomposes at 187°, after sintering at 155°. Sometimes it crystallized in needles which frothed at 150–153°, after sintering at 140°.

0.1254 gr. subst. became 0.1161 gr. after being dried in a vacuum at 80°, and gave 0.0715 gr. AgCl. 8.74 mg. subst. gave 0.425 c.c. nitrogen (12,° 755.4 mm.) (Found: H_2O=7.42, Cl=14.11, N=5.83. $C_{11}H_{14}O_2NCl.H_2O$ requires H_2O=7.34, Cl=14.44, N=5.70 %).

The iodide is readily obtained by the action of potassium iodide on the aqueous solution of the chloride; decomp. p. 213° (corr. 218°).[1]

0.1127 gr. subst. gave 0.0820 gr. AgI. 5.85 mg. subst. gave 4.28 mg. AgI (methoxyl). (Found: I=39.33, CH_3O−=9.67. (CH_3O)-$C_{10}H_{11}ONI$ requires I=39.78, CH_3O− =9.72 %).

---

(1) Compare F. L. Pyman, *J. Chem. Soc.*, **97** (1910), 278.

The perchlorate crystallizes in white needles, which melt at 196–197°.

6-Methoxy-7-hydroxy-2-methyl-3·4-dihydroisoquinolinium salts dissolve in dilute alkali to deep yellow solutions, which on a further addition of a concentrated solution of caustic alkali become colourless, and, on dilution with water, regain their colour. The picrate of this base shows peculiar phenomena ; the aqueous solution of the chloride, when mixed with aqueous picric acid first deposits yellow needles, which on being gently heated, or on standing for several hours, are converted into orange-red prisms, and these when left standing for many days, or on being boiled with water,—but in not sufficient quantity to dissolve them all—, once more turn to yellow granular crystals. The orange-red modification contains one molecule of the water of the crystallization ; m. p. 92°.

0.1522 gr. subst. became 0.1465 gr. after being dried in a vacuum at 56°. (Found : H_2O=4.19. $C_{17}H_{16}O_9N_4 \cdot H_2O$ requires H_2O=4.11 %).

The yellow granular modification is the most stable and anhydrous ; m. p. 159–160°.

0.0787 gr. subst, gave 0.1396 gr. CO_2 and 0.0296 gr. H_2O. (Found : C=48.38, H=4.21. $C_{17}H_{16}O_9N_4$ requires C=48.55, H=3.84 %).

6·7-Dihydroxy-2-methyl-3.4-dihydroisoquinolinium Chloride (IX). 2 grams of hydrostinine and 5 grams of phosphorus pentachloride were heated in a sealed tube at 145–150° for five hours. After being cooled to room temperature, the tube was opened and 10 c.c. of alcohol was poured in, when a copious evolution of gas took place and 6·7-dihydroxy-2-methyl-3·4-dihydroisoquinolinium chloride separated as a yellow crystalline powder. This was purified by recrystallization from glacial acetic acid, from which it was deposited in anhydrous prisms, decomp. p. 268° (corr. 276°). All its properties are in agreement with the description given by Pyman.(1)

0.1467 gr. subst. gave 0.0993 gr. AgCl. (Found : Cl=16.75. $C_{10}H_{12}O_2NCl$ requires Cl=16.60 %).

On addition of sodium carbonate to a concentrated solution of chloride IX, the phenolbetaine of 6·7-dihydroxy-2-methyl-3·4-dihydroisoquinolinium hydroxide separates in deep yellow glistening leaflets. The same compound is also obtained from compound VIII in the same way as was done by Pyman from 6·7-dimethoxy-2-methyl-3·4-dihydroisoquinolinium chloride.

Action of Methyl Iodide on the Phenolbetaine of 6·7-Dihydroxy-2-methyl-3·4-dihydroisoquinolinium-hydroxide. 1 gram of finely powdered anhydrous phenolbetaine and 3 grams of methyl iodide were heated together in a sealed tube for 3 hours at 100°. The product was dissolved in water, treated with a concentrated solution of potassium iodide, when 6-

(1) Pyman, loc. cit., p. 273.

methoxy-7-hydroxy-2-methyl-3·4-dihydroisoquinolinium iodide separated as yellow crystals (0.6 gram). It was easily purified by recrystallization from alcohol ; decomp. p. 213° (corr. 218°).

8.79 mg. subst. gave 6.45 mg. AgI. 6.92 mg. subst. gave 4.95 mg. AgI (methoxyl). (Found : I=39.66, CH_3O- =9.45. (CH_3O)-$C_{10}H_{11}ONI$ requires I=39.78, CH_3O-=9.72 %).

The chloride was prepared by digesting the alcoholic solution of the iodide with freshly precipitated silver chloride ; decomp. p. 187°. When the picrate (m. p. 159–160°) was mixed with the picrate of synthesized 6-methoxy-7-hydroxy-2-methyl-3·4-dihydroisoquinolinium base, no depression of the melting point occurred.

6-Benzyloxy-7-hydroxy-2-methyl-3·4-dihydroisoquinolinium iodide (XI). 1.6 grams of phenolbetaine and 3 grams of benzyl iodide were heated together for half an hour on a bath of boiling water. The excess of benzyl iodide was removed by trituration with absolute ether. After fractional crystallization from hot water, two compounds were isolated from the product ; the one is readily soluble in hot water, while the other is only slightly soluble. The former is soluble in dilute alkali to a deep yellow solution, a behaviour exactly similar to that of 6-methoxy-7-hydroxy-2-methyl-3·4-dihydroisoquinolinium salt. The result of analysis agreed with 6-benzyloxy-7-hydroxy-2-methyl-3·4-dihydroisoquinolinium iodide; m. p. 189–190°. Yield 1.5 grams.

16.15 mg. subst. gave 9.53 mg. AgI. (Found : I=31.90. $C_{17}H_{18}O_2NI$ requires I=32.11 %).

The latter is insoluble in alkali, and is nothing but 6·7-dibenzyloxy-2-methyl-3·4-dihydroisoquinolinium iodide ; m.p. 194–195°. Yield 0.5 gram.

13.85 mg. subst. gave 6.68 mg. AgI. (Found : I=26.07. $C_{24}H_{24}O_2NI$ requires I=26.18 %).

6-Benzyloxy-7-(6-benzyloxy-7-hydroxy-2-methyl-3·4-dihydroisoquinoliniumoxy)-2-methyl-3·4-dihydroisoquinolinium Iodie (XII). When a concentrated solution of compound XI was treated with potassium carbonate, orange coloured oily drops were deposited, which on standing for many days, were converted into orange prisms. After recrystallization from alcohol it melted at 196–198°. This still contains iodine, and is assumed to have the constitution of XII.

11.26 mg. subst. gave 4,02 mg. AgI. (Found : I=19.30. $C_{17}H_{18}O_2N$-O-$C_{17}H_{17}ONI$ requires I=19.16 %).

6-Benzyloxy-7-hydroxy-2-methyl-3·4-dihydroisoquinolinium Salts (XIII.) The mixture of 1 gram of the above mentioned compound (XII) and 0.5 gram of methyl iodide was left at room temperature for one day. At the end of the reaction the orange colour changed to a pale yellow. The product

was dissolved in water, treated with a concentrated solution of sodium hydroxide, and extracted with ether. The ethereal solution was shaken with water containing a little hydrochloric acid, whereby the aqueous layer exhibited a green fluorescence. On addition of picric acid to this aqueous solution, precipitation of yellow crystalline picrate took place. After repeated crystallization from alcohol this picrate formed yellow leaflets, which melted at 176–177°. On mixing with 6-methoxy-7-benzyloxy-2-methyl-3•4-dihydroisoquinolinium picrate, it melted at 150–160°.

6.11 mg. subst. gave 0.554 c. c. nitrogen (22°, 761 mm.) (Found : N= 10.74. $C_{24}H_{22}O_9N_4$ requires N=10.98 %).

The perchlorate crystallizes in beautiful needles exhibiting a green fluorescence. This is almost insoluble in water but moderately soluble in alcohol ; m. p. 222–225°.

ClO_4 in perchlorates was estimated as nitron perchlorate, according to the method of Fichter and Schmidt.[1] In filtering and weighing the precipitate, Pregl's microfiltering tube was employed with good results. The accuracy of this method was confirmed in the case of several known substances.

12.78 mg. subst. gave 14.01 mg. $C_{29}H_{16}O_4$•$HClO_4$. (Found : ClO_4=26.42. $C_{18}H_{29}O_2NClO_4$ requires ClO_4=26.06%);

6-Hydroxy-7-methoxy-2-methyl-3•4-dihydroisoquinolinium Salt (XIV). 15 milligrams of 6-benzyloxy-7-methoxy-2-methyl-3•4-dihydroisoquinolinium perchlorate were treated with 2 c. c. of concentrated hydrochloric acid. After the crystals had all dissolved, the solution was evaporated in a vacuum, and the residue was crystallized from alcohol, from which it separated in the form of slightly brownish coloured, spear-head-like crystals, m. p. 178–179.5°. Yield 10 milligrams. This is easily soluble in alcohol or water to light yellow greenish fluorescent solutions. With ferric chloride the solutions give no colouration.

7.12 mg. subst. gave 10.19 mg. $C_{21}H_{16}N_4$•$HClO_4$. (Eound : ClO_4=34.50. $C_{11}H_{14}O_2NClO_4$ requires ClO_4 =34.11%).

The writer wishes to express his sincere thanks to Professor Dr. R. Majima and Dr. S. Kobayashi for their kind guidance and continued encouragement during the course of this work.

(The end)

Chemical Institute, Tohoku Imperial University, Sendai.

---

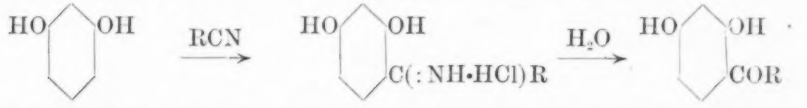
(1) *Z. anorg. Chem.*, 98 (1916), 142.

THE CONDENSATION OF RESORCINOL WITH ETHYLENE DICYANIDE.

By Junkichi MURAI.

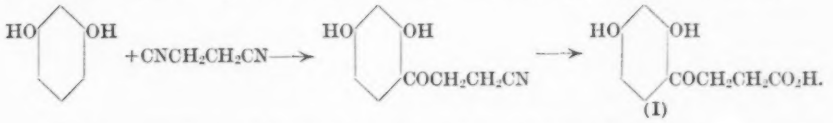
Received April 20, 1926. Published June 28, 1926.

Since Hoesch[1] first discovered that nitriles reacted with certain phenols, in the presence of anhydrous zinc chloride and dry hydrogen chloride, to give aromatic hydroxy-ketones according to the following scheme :



this reaction has been applied extensively in the preparation of carbonyl compounds. Sonn'[2] applied this method to a dicyanide and found that o-cyanoacetyl phloroglucinol, $CNCH_2CO{\cdot}C_6H_2(OH)_3$, and 2:4:6:2′:4′:6′-hexahydroxydibenzoylmethane, $C_6H_2(OH)_3COCH_2COC_6H_2(OH)_3$, were obtained by the condensation of malonitrile with phloroglucinol.

With the view of synthesising phenolic γ-diketones, the author attempted to condense resorcinol with ethylene dicyanide by Hoesch's method. However, the action of ethylene dicyanide on resorcinol resulted in the production of a compound, which, from its composition and method of formation, was regarded as β-2:4-dihydroxybenzoylpropionic acid (I) :



(I)

The constitution of this acid was confirmed beyond doubt by the preparation of its salt, and by the formation of the dibenzoyl derivative and of the oxime of the dimethyl derivative.

Experimental.

Synthesis of β-2:4-Dihydroxybenzoylpropionic Acid, $C_6H_3(OH)_2COCH_2CH_2CO_2H$. (a) Twenty two grams of resorcinol (2 mols) and 8 grams of ethylene dicyanide (1 mol) were dissolved in absolute ether (100 c. c.) and, after the addition of 8 grams of freshly fused and powdered zinc chloride, a gentle stream of dry hydrogen chloride was passed into the liquid for four hours, the mixture being kept warm during this operation, when a red syrup

(1) *Ber.*, **48** (1915), 1122.
(2) *Ber.*, **50** (1917), 1292.

separated. After allowing to remain overnight and decanting the ether, the syrup was dissolved in 150 grams of ice-cold water, concentrated to about 100 c. c. on the water-bath and then cooled. The dark brown substance thus separated was crystallised once from water with the addition of animal charcoal, when it separated in grey crystals melting at 197–199.° The yield was 5.7 grams. As it is difficult to obtain these crystals so that they are free from any mineral matter by further recrystallisation, the acid was converted into its sodium salt, and, after recrystallising from water, the salt was acidified with hydrochloric acid, in order to regenerate the free acid, and again recrystallised several times from water. It was colourless crystals melting at 199–200°:

4.297 mg. subst. gave 9.020 mg. CO_2 and 1.966 mg. H_2O. (Found: C=57.25; H=5.12. $C_{10}H_{10}O_5$ requires C=57.12; H=4.80%).

(b) Since the interaction between resorcinol (2 mols) and ethylene dicyanide (1 mol) resulted in the formation of β-2:4-dihydroxybenzoylpropionic acid, the condensation was again carried out under the same conditions as in (a), except that 11 grams of resorcinol (1 mol) were used. The yield of β-2 : 4-dihydroxybenzoylpropionic acid was 5.7 grams after once crystallising from water.

The Sodium Salt. For the preparation of this salt, 3 grams of the crude β-2:4-dihydroxybenzoylpropionic acid were shaken with a concentrated solution of sodium carbonate until the evolution of carbon dioxide had ceased. The salt thus obtained was collected and recrystallised from small quantity of water, when it separated in colourless crystals (yield 3.9 grams). The air-dried salt lost 18.53% in weight when heated at 130° under reduced pressure. The anhydrous salt gave, on analysis, the following results:

5.154 mg. subst. gave 1.282 mg. Na_2SO_4 and 4.347 mg. subst. gave 1.102 mg. Na_2SO_4. (Found: Na=8.05 and 8.21. $C_{10}H_9O_5Na{\cdot}3H_2O$ requires H_2O=18.89; Na=8.04%.)

The Benzoyl Derivative One gram of β-2:4-dihydroxybenzoylpropionic acid was dissolved in 5.5 c.c. of a 10% solution of sodium hydroxide and shaken with 1.1 c.c. of benzoyl chloride for two hours. After acidifying with dilute hydrochloric acid, the precipitate was collected, washed with water and dried (yield 1.3 grams). It crystallised from dilute methyl alcohol in colourless crystals, m. p. 146–147°:

4.698 mg. subst. gave 11.840 mg. CO_2 and 1.931 mg. H_2O. (Found: C=68.73; H=4.59. $C_{24}H_{18}O_7$ requires C=68.88; H=4.34%).

β-2:4-Dimethoxybenzoylpropionic Acid, $C_6H_3(OCH_3)_2COCH_2CH_2CO_2H$. β-2:4-Dihydroxybenzoylpropionic acid (5 grams) was dissolved in 25 c.c. of a 10% sodium hydroxide and shaken with 4.5 c.c. of methyl sulphate for two hours, when a small quantity of oil deposited, which was extracted with

ether. The aqueous residue (A) and the ethereal extract (B) were treated in the following way.

The aqueous residue (A) was acidified with dilute hydrochloric acid and the precipitate was collected, washed with water and dried. After recrystallising several times from methyl alcohol with the addition of animal charcoal, it separated in colourless crystals and melted at 124–125.° The yield was 4.5 grams after one crystallisation.

The ethereal extract (B) was washed with water until free from alkali. After the evaporation of the ether, the residual oil was hydrolysed by warming it with a dilute solution of sodium hydroxide and the alkaline solution was acidified with hydrochloric acid. The precipitate was collected, washed with water, dried, and recrystallised from alcohol, when it melted at 124–125° and produced no depression of the melting point by admixture with β-2:4 dimethoxybenzoylpropionic acid:

4.645 mg. subst. gave 10.262 mg. CO_2 and 2.473 mg. H_2O. (Found: C=60.25; H=5.96. $C_{12}H_{14}O_5$ requires C=60.48; H=5.93 %).

The Oxime. A mixture of β-2:4-dimethoxybenzoylpropionic acid (0.2 gram), hydroxylamine hydrochloride (0.06 gram) and sodium acetate (0.12 gram) was dissolved in dilute alcohol and boiled for two hours under a reflux condenser. After the removal of the alcohol, the oxime separated, which crystallised from dilute methyl alcohol as colourless crystals melting at 155–156.° The quantity of the crude oxime amounted to 0.2 gram:

6.516 mg. subst. gave 0.307 c. c. nitrogen at 13° and 755.3 mm. (Found: N=5.59. $C_{12}H_{15}O_5N$ requires N=5.53%).

In conclusion, the author wishes to express his hearty thanks to Dr. Hiroshi Nomura, in whose laboratory this investigation was carried out.

Chemical Institute, Faculty of Science,
Tohoku Imperial University, Sendai.